REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	**2. REPORT TYPE**	**3. DATES COVERED** *(From - To)*
April 2012	Viewgraph	April 2012- June 2012

4. TITLE AND SUBTITLE
Volatilization mechanism of 1-ethyl-3-methylimidazolium bromide ionic liquid

5a. CONTRACT NUMBER
In-House

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

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5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER
23031166

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

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8. PERFORMING ORGANIZATION REPORT NO.

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
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AFRL/RQR
5 Pollux Drive
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10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AFRL-RZ-ED-VG-2012-200

12. DISTRIBUTION / AVAILABILITY STATEMENT
Distribution A: Approved for Public Release; Distribution Unlimited. PA#12466

13. SUPPLEMENTARY NOTES
Conference paper for the 22nd International Symposium on Gas Kinetics, Boulder, CO in 18-22 June 2012.

14. ABSTRACT

Although molten salts, more recently known as ionic liquids (ILs), have been known for almost a century (for instance, ethylammonium nitrate, mp =12 °C, was discovered in 1914),**1** the rapid development of ionic liquid chemistry has only occurred within the last decade. In 2000, only 217 papers were published on the subject, whereas in 2010, over 6,000 papers appeared in the literature. The number of possible ILs has been estimated at 1018.**3** Detailed studies of ILs offer insight into new and more complex fundamental chemistry, as well as allow for an assessment for their potential application in emerging technologies such as in solar cells, fuel electrolytes, bio- or nano-catalysts, high-energy-density propellants, and green solvents. In order to better understand the volatilization process for ILs, the vapor evolved from heating the ionic liquid 1-ethyl-3-methylimidazolium bromide (EMIM+Br-) was analyzed via tunable vacuum ultraviolet photoionization time of flight mass spectrometry (VUV-PI-TOFMS) and thermal gravimetric analysis mass spectrometry (TGA-MS). For this ionic liquid, the experimental results indicate that vaporization takes place via the evolution of alkyl bromides and alkylimidazoles, presumably through alkyl abstraction via an SN2 type mechanism, and that vaporization of intact ion pairs or the formation of carbenes is negligible. Activation enthalpies for the formation of the methyl and ethyl bromides were evaluated experimentally, □H.‡(CH3Br) = 116.1±6.6 kJ/mol and □H.‡(CH3CH2Br) = 122.9±7.2 kJ/mol, and the results are found to be in agreement with calculated values for the SN2 reactions. Comparisons of product photoionization efficiency (PIE) curves with literature data are in good agreement, and *ab initio* thermodynamics calculations are presented as further evidence for the proposed thermal decomposition mechanism. Estimates for the enthalpy of vaporization of 1- ethyl-3-methylimidazolium bromide and, by comparison, 1-butyl-3-methylimidazolium bromide (BMIM+Br-) from molecular dynamics calculations and their gas phase enthalpies of formation obtained by G4 calculations yield estimates for the ionic liquids.' enthalpies of formation in the liquid phase: □Hvap(298 K) (EMIM+Br-) = 168±20 kJ/mol, □Hf, gas(298 K) (EMIM+Br-) = 38.4±10 kJ/mol, □Hf, liq(298 K) (EMIM+Br-) = -130±22 kJ/mol, □Hf, gas(298 K) (BMIM+Br-) = -5.6±10 kJ/mol, and □Hf, liq(298 K) (BMIM+Br-) = -180±20 kJ/mol.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
					Tommy Hawkins
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**	SAR	16	**19b. TELEPHONE NO** *(include area code)*
Unclassified	**Unclassified**	**Unclassified**			661-275-5449

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. 239.18

Volatilization Mechanism of 1-Ethyl-3-methylimidazolium Bromide Ionic Liquid

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Acknowledgements

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Jerry Boatz

ALS/UC Berkeley:

Christine Koh

Oleg Kostko

Amir Golan

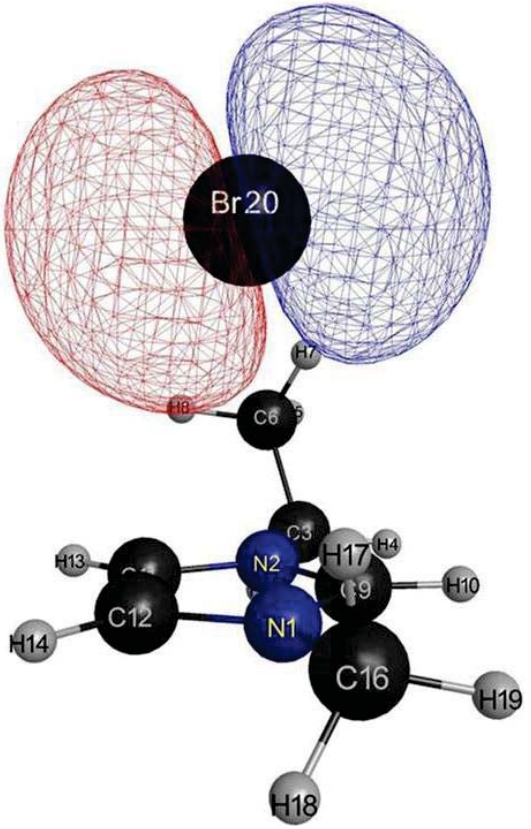
Stephen Leone

AFOSR:

Mike Berman

Motivation to Study Room Temperature Ionic Liquids

- Molten Salts @ RT
  - Low mp
  - Large (organic) ions
  - Low volatility ($vp_{298\ K}$ << 1 Pa)
  - Thermally stable
  - Good conductivity
  - Good solvents
  - Unique reactivity
- Popularized in green/sustainable chemistry applications



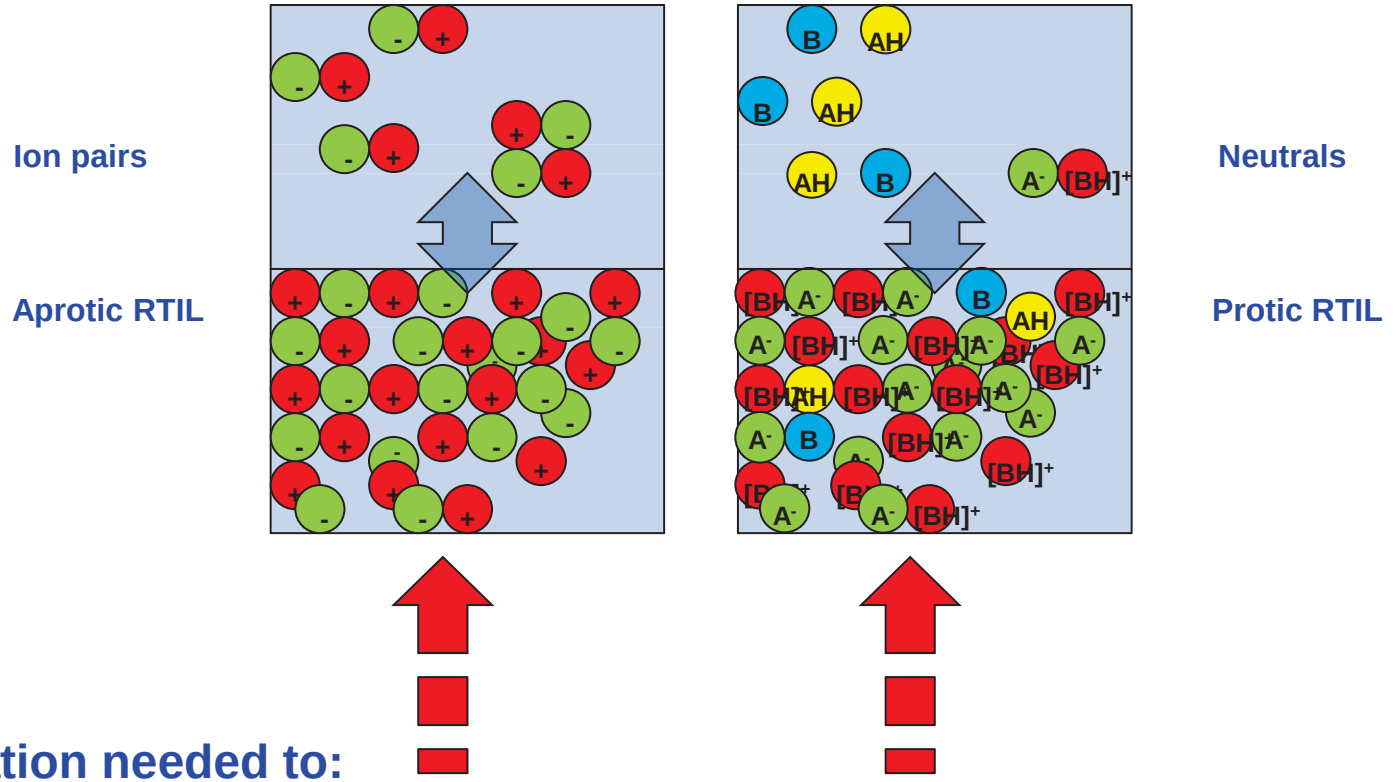
- > 10^{18} cation/anion pair combinations
- Enormous tunability

Hypergolic Ignition

- Autoignition at ambient P & T
  - MMH/NTO current hypergol propellants
- IL hypergol fuels low vapor toxicity
  - Operational cost savings (cf MMH)
- Higher performing than MMH
  - Synthesis tunability
- T_b (calculated) >> T_d for ILs
  - What role does decomposition/vaporization play in understanding IL/ox autoignition?

JPC-A **2008**, *112*, 7816

How Do ILs Volatilize?



Information needed to:

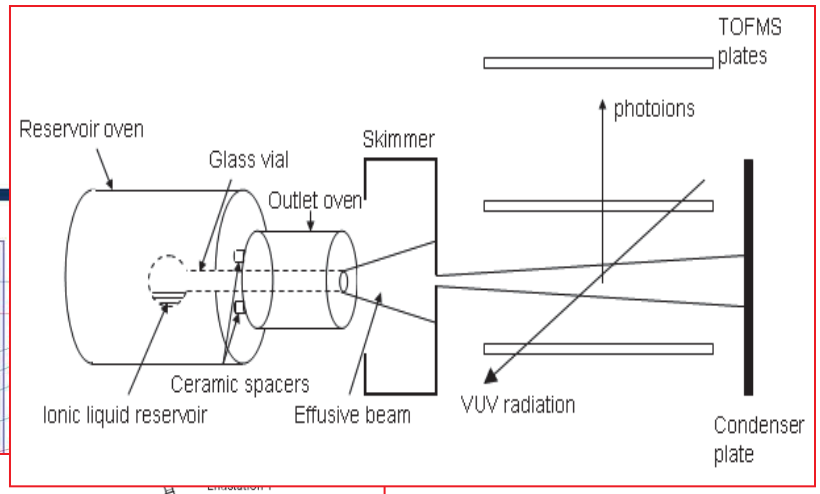
- ❑ Understand gas phase structure of ILs
- ❑ Determine heat of vaporization….. calibrate MD simulations
- ❑ (for $\Delta H_{f(l)}$ and therefore I_{sp})

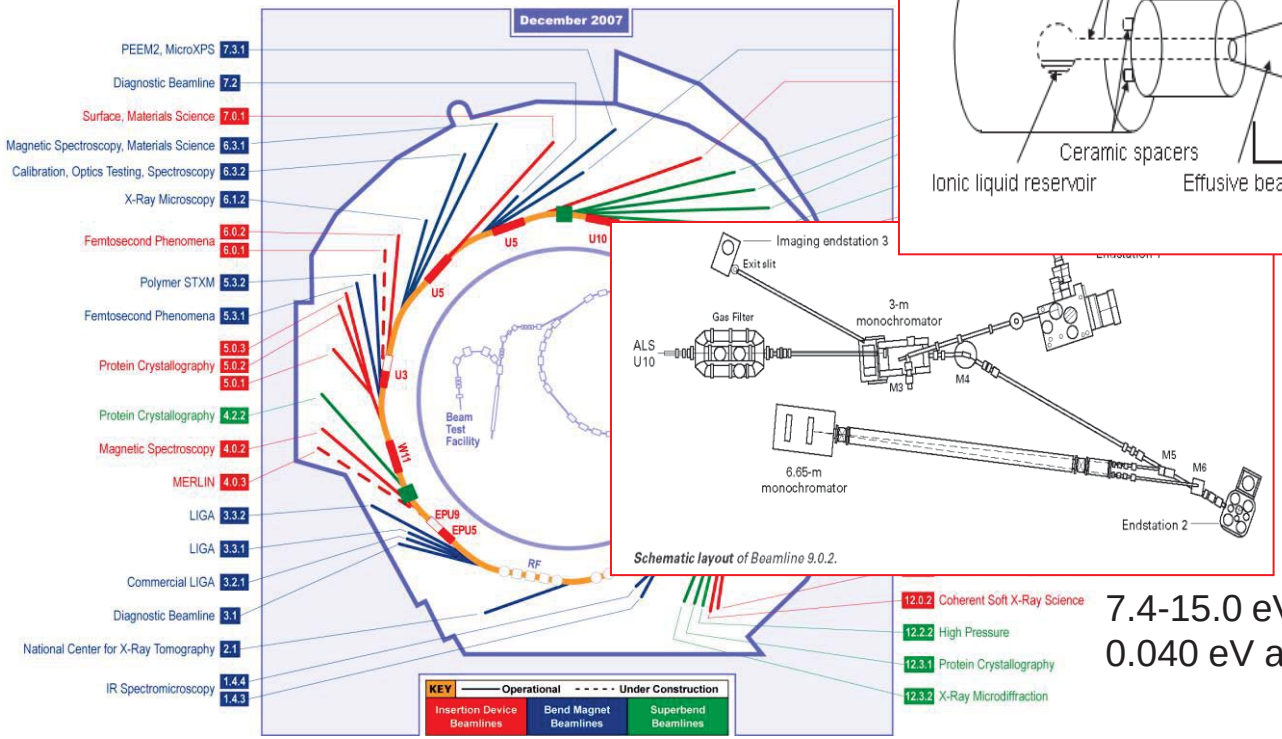
- ❑ Characterize thermal decomposition of ILs (basicity & nucleophilicity of anion)

Probing Ionic Liquid Vapor by VUV Photoionization Mass Spectrometry

Effusive Vapor Source

Separate temperature control of reservoir and outlet

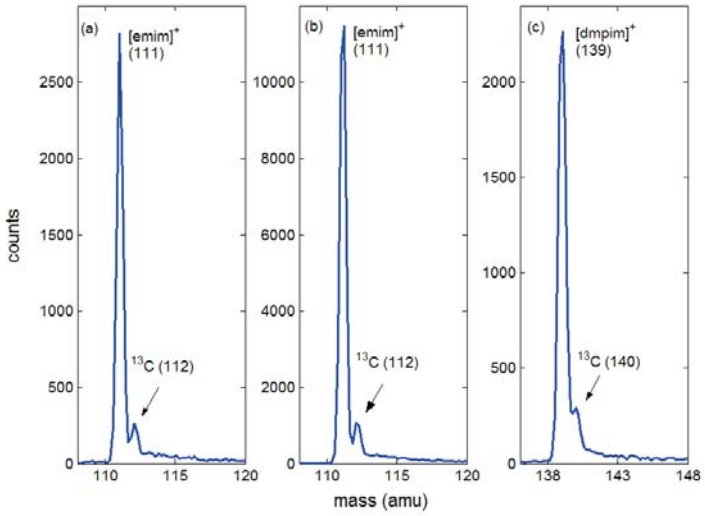


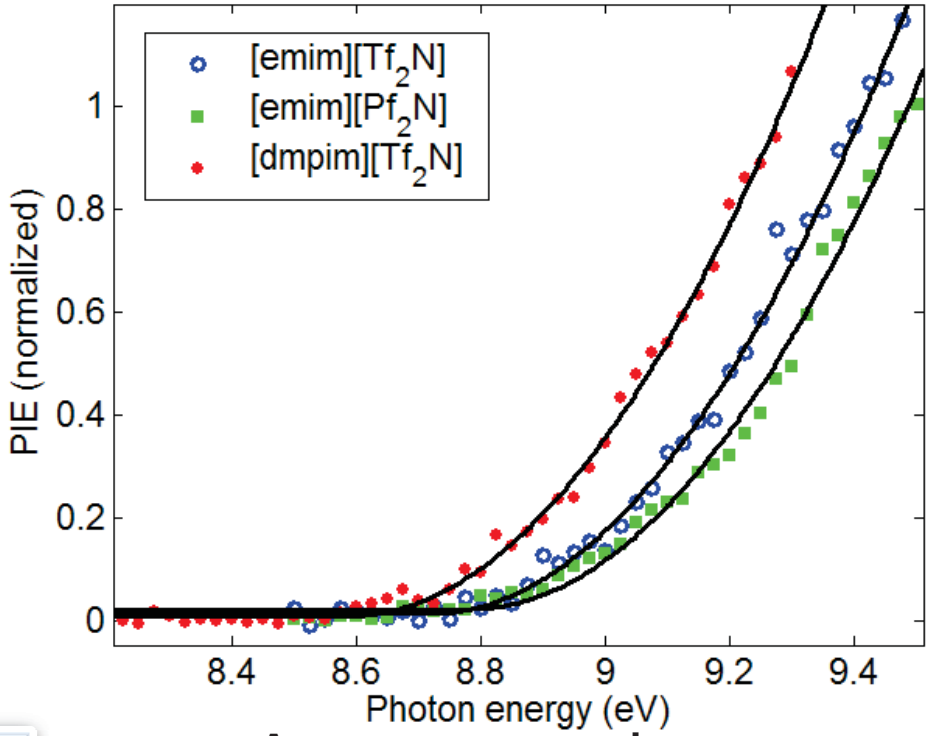


7.4-15.0 eV photons, 0.025 eV resolution, 0.040 eV absolute accuracy

Structure of Aprotic ILs in the Gas Phase

- PIE curves and structures





Appearance energies are:

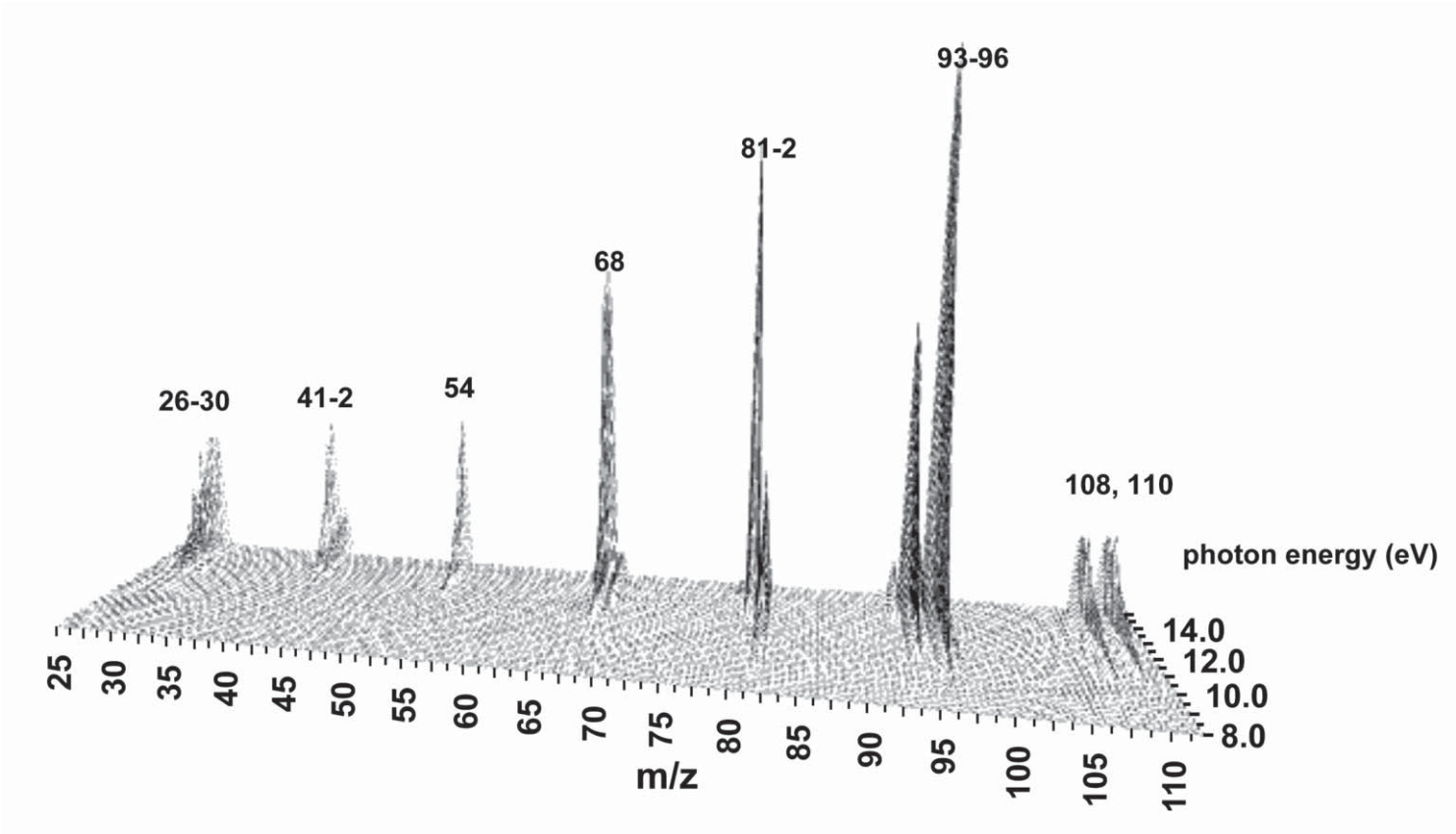
[emim][Tf_2N]: 8.72 ± 0.03 eV
[emim][Pf_2N]: 8.78 ± 0.04 eV
[dmpim][Tf_2N]: 8.59 ± 0.03 eV

- Dissociative photoionization

$C^+A^- + h\nu \rightarrow C^+A + e^- \rightarrow C^+ + A + e^-$

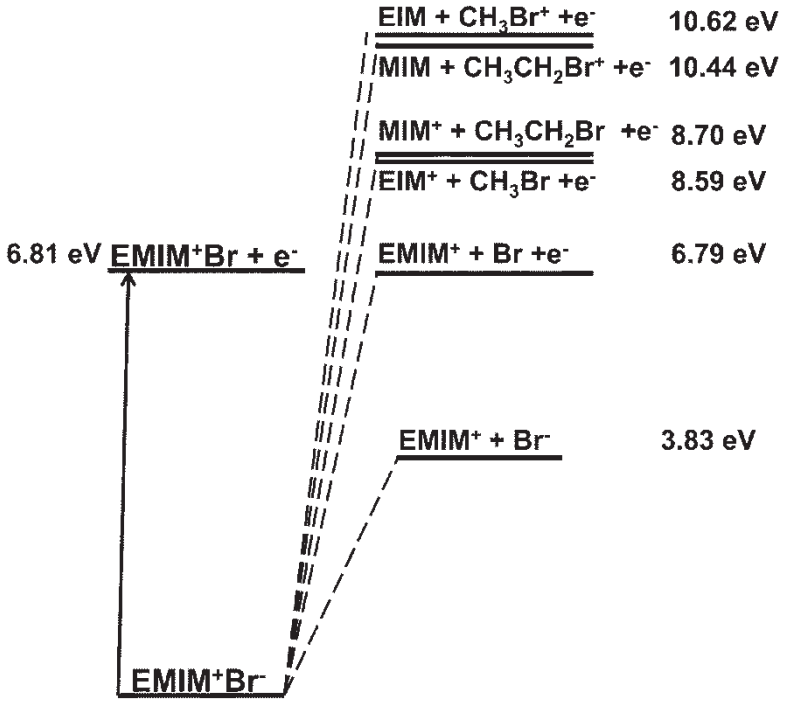
JPC-A **2010,** *114*, 879

Volatilization of $EMIM^+Br^-$



- No ion signal at 111
  - No gas phase IL ion pairs
  - No dissociative ionization of IL ion pairs
  - New process for volatilization

Photoionization Energetics of Gas Phase $EMIM^+Br^-$



Is this responsible for 94 & 96 ion masses?

Is this responsible for 108 & 110 ion masses?

Is this responsible for 82 ion mass?

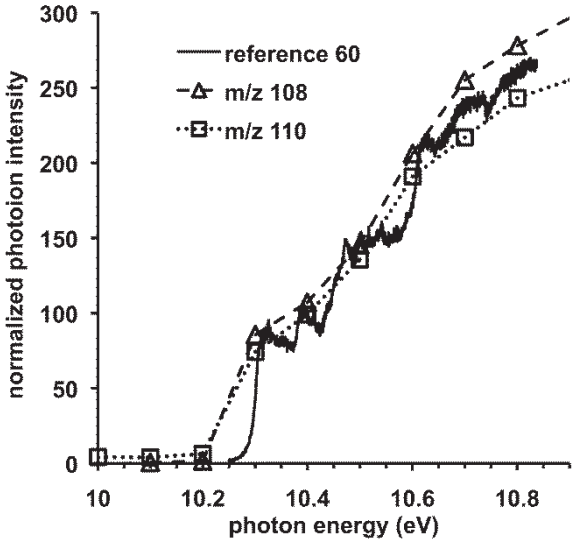
Is this responsible for 96 ion mass?

No 111 ion mass

How would you go about detecting this channel?

MP2/6-31+G(d,p), 0 K, ZPVE corrected

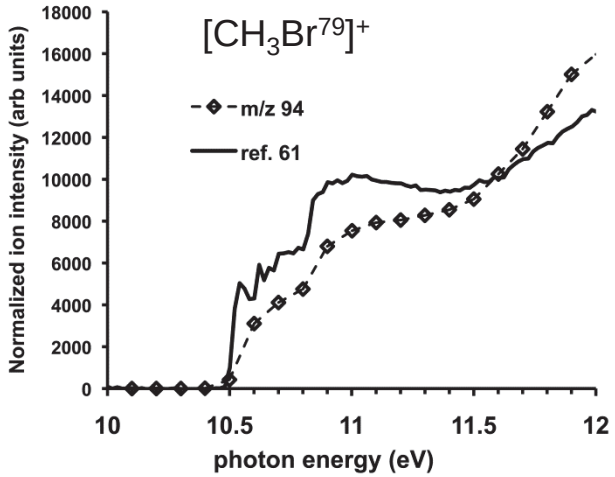
Photoionization Efficiency (PIE) Curves

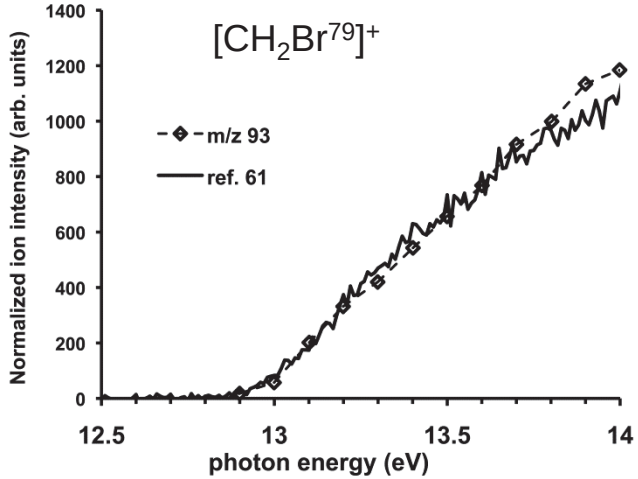


$[CH_3CH_2Br^{79,81}]^+$

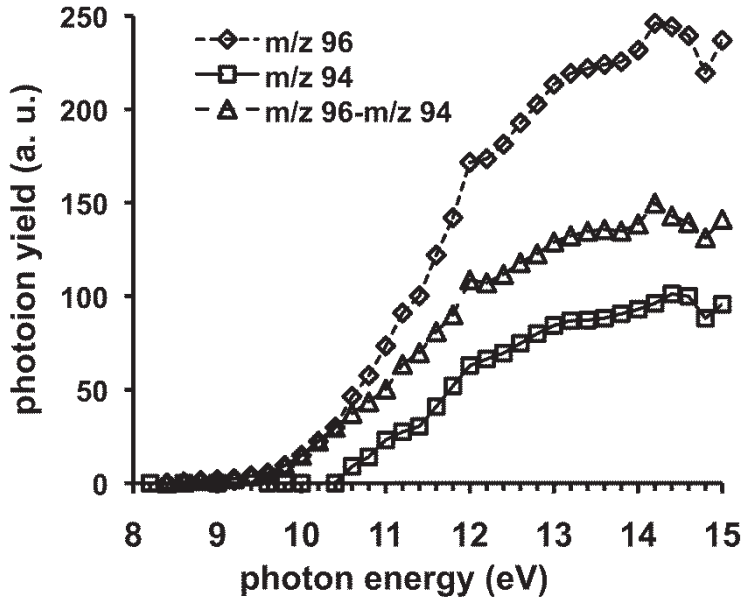
Ref 60:
Baer, T.; Song, Y.; Liu, J.; Chen, W.; Ng, C. Y. *Faraday Discuss.* **2000**, *115*, 137

Ref 61:
Locht, R.; Leyh, B.; Dahareng, D.; Hottmann, K.; Jochims, H. W.; Baumgartel, H. *Chem. Phys.* **2006**, *323*, 458





Photoionization Efficiency (PIE) Curves



$EIM^+ + [CH_3Br^{81}]^+$

EIM^+ only

$[CH_3Br^{79}]^+$

All experimental AEs consistent with MP2 values for dissociative photoionization of IL ion pair but no 111 ion mass

Is there another explanation?

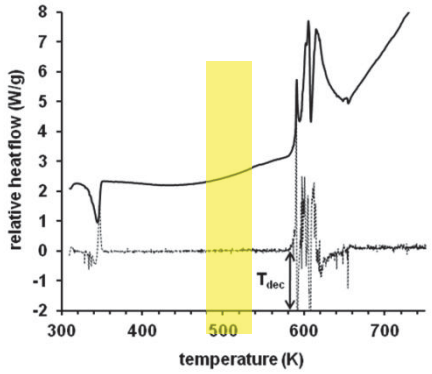
Thermolysis of $EMIM^+Br^-$ can Explain observed PIE curves

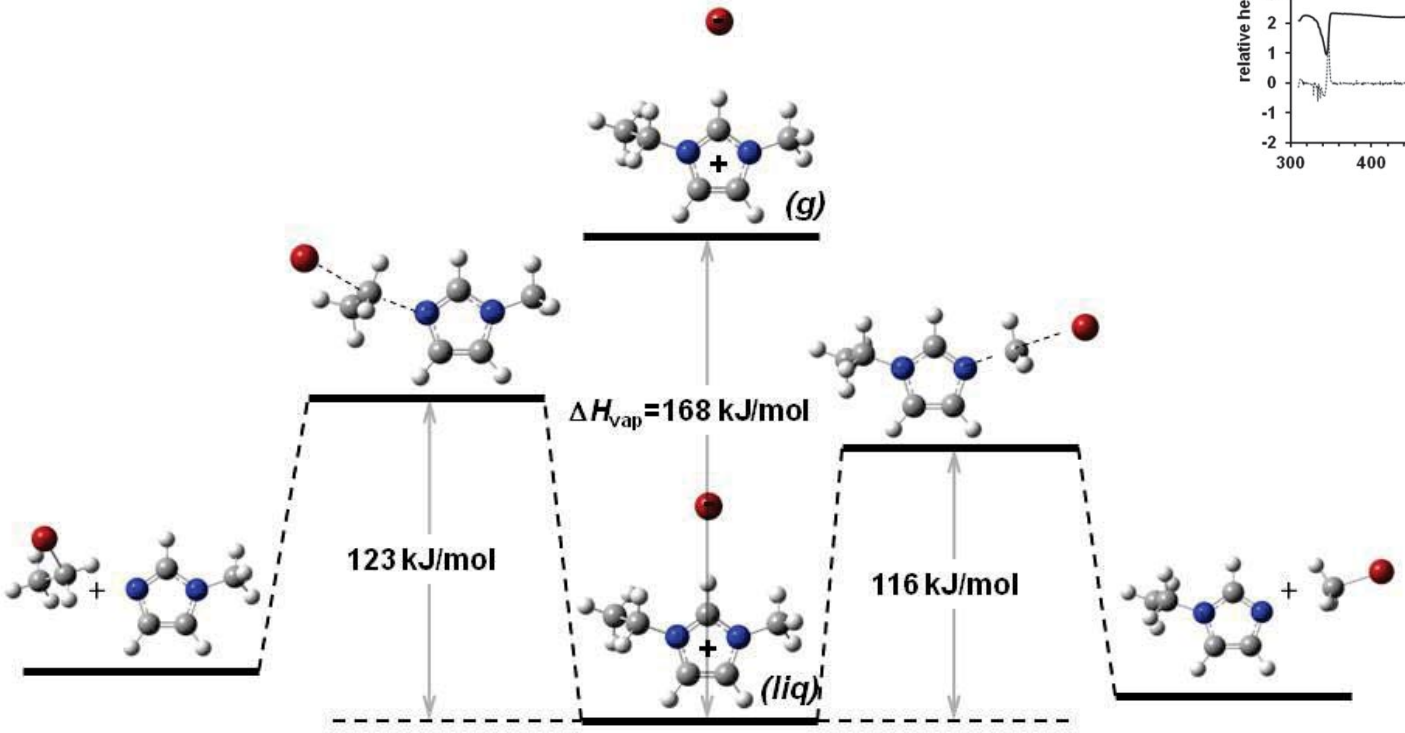
$EMIM^+Br^-_{(l)} \rightarrow CH_3Br_{(g)} + EIM_{(g)}$

$EMIM^+Br^-_{(l)} \rightarrow CH_3CH_2Br_{(g)} + MIM_{(g)}$

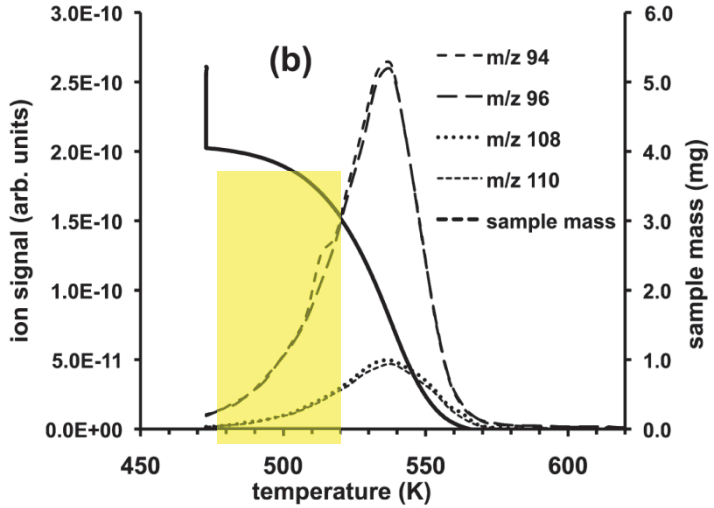
Observed AEs consistent with experimental/MP2/6-31+G(d,p) IEs

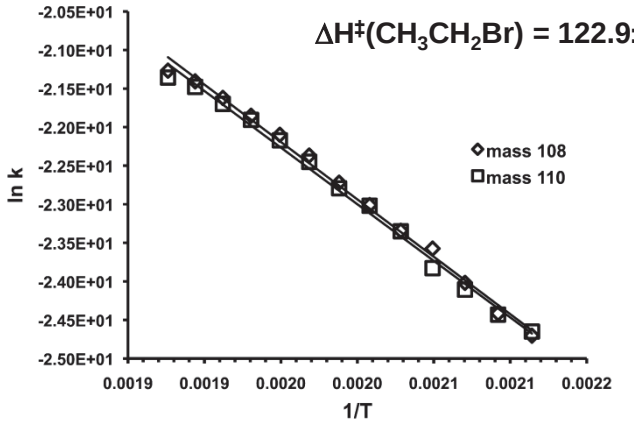
VUV beamline is sampling thermolysis not vaporization products

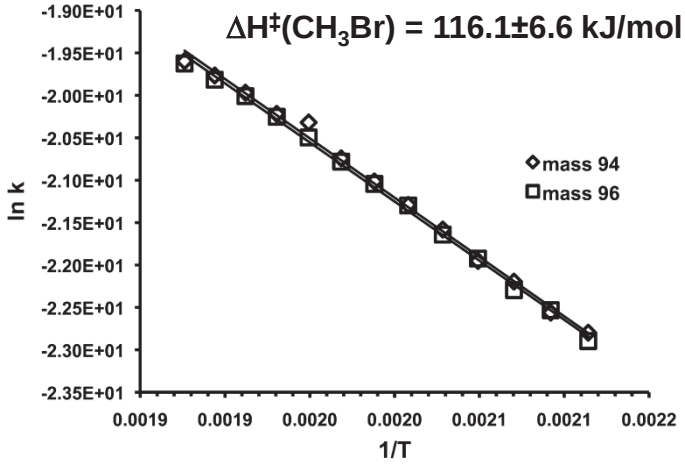




TGA/MS Analysis of $EMIM^+Br^-$ Thermolysis







ΔH_{vap} for $EMIM^+Br^-$ & $BMIM^+Br^-$

MD values

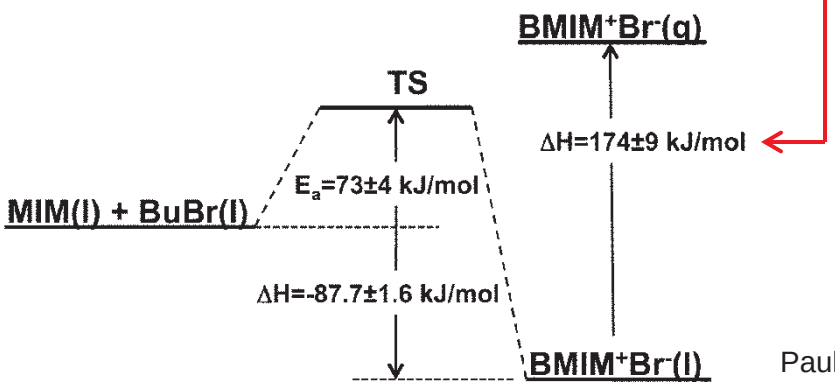
	T (K)	ΔH_{vap} (kJ/mol)
$EMIM^+Br^-$	298	147.1[b]
$EMIM^+Br^-$	393	138.3[a]
$EMIM^+Br^-$	473	130.8[a]
$BMIM^+Br^-$	298	152.8[b]
$BMIM^+Br^-$	323	150.5[a]
$BMIM^+Br^-$	393	144.0[a]

[a] MD direct calculation. [b] Linear extrapolation from higher temperature MD values.

298 K values, this study

$\Delta H_{vap}(EMIM^+Br^-)$ = 168 ± 20 kJ/mol
$\Delta H_{f,\ gas}(EMIM^+Br^-)$ = 38.4 ± 10 kJ/mol
$\Delta H_{f,\ liq}(EMIM^+Br^-)$ = -130 ± 22 kJ/mol
$\Delta H_{f,\ gas}(BMIM^+Br^-)$ = -5.6 ± 10 kJ/mol
$\Delta H_{f,\ liq}(BMIM^+Br^-)$ = -180 ± 20 kJ/mol

Calorimetric / *ab initio* values



Paulechka, Y. U.; Kabo, A. G.; Blokhin, A. V. *J. Phys. Chem. B* **2009**, *113*, 14742

Conclusions

- VUV PI ToF MS spectroscopy has provided
  - Structural information on volatilized species from ILs
  - AEs & PIE curves, which leads to unique identification
  - ΔH_{vap}, which leads to ΔH_{liq} & allows MD calibrations
  - Insight into the dynamics of dissociative photoionization
- Nature of the IL volatiles are cation/anion dependent
  - Ion pairs
  - Neutrals from proton transfer
  - Neutrals from decomposition
- IL combustion is influenced by the nature of the volatiles (fuel)